(12) UK Patent Application (19) GB (11) 2 334 529 (13) A

(43) Date of A Publication 25.08.1999

(21) Application No 9904022.2

(22) Date of Filing 22.02.1999

(30) Priority Data
(31) 09027662 (32) 23.02.1998 (33) US

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(51) INT CL^6
C10M 155/02

(52) UK CL (Edition Q)
C5F FKG F102 F139
U1S S1364

(56) Documents Cited
GB 2072691 A
WPI Abstract Accession No 85-259382/42 & JP600172315 (SHINETSU CHEM IND) See abstract
WPI Abstract Accession No 88-252628/25 & JP630182008 (SHINETSU CHEM IND) See abstract

(58) Field of Search
UK CL (Edition Q) C5F FKG
INT CL^6 C10M 155/02
ONLINE:CAS-ONLINE, EPODOC, JAPIO, WPI

(54) Abstract Title

Storage stable lubricant additive concentrate containing an antifoaming agent and methods of making the same

(57) The present invention relates to a method for making a storage stable lubricant additive concentrate containing a silicone antifoaming agent. The method utilizes a high-speed in-line mixer to impart hydraulic and mechanical shear to the lubricant additive concentrate, resulting in improved dispersion of the antifoaming agent within the concentrate. The lubricant additive concentrate produced is storage stable, and when diluted with an oil of lubricating viscosity, results in lubricants and functional fluids having improved antifoaming properties. The silicone antifoaming agent and remaining ingredients of the concentrate form a micro-emulsion.

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STORAGE STABLE LUBRICANT ADDITIVE CONCENTRATE CONTAINING AN ANTIFOAMING AGENT AND METHODS OF MAKING THE SAME

The present invention relates to a storage stable lubricant additive concentrate, and methods of making the same. The storage stable lubricant additive concentrate made according to the present invention is added to a major amount of an oil of lubricating viscosity to produce lubricant compositions or functional fluids having improved antifoaming properties.

Background of the Invention

Lubricants or functional fluids provide protection for equipment by reducing and/or preventing harmful metal to metal contact and oxidation. These lubricants or functional fluids perform many functions, including lubrication, power transmission, hydraulic transfer, and the like. Examples of functional fluids include manual and automatic transmission fluids, power steering fluids, hydraulic fluids and farm tractor fluids. A lubricating composition's ability to perform these functions is reduced when foaming occurs in the lubricating composition.

Silicone antifoaming agents have been used in the past to reduce or control foaming in lubricants or functional fluids. Lubricant additive concentrates made with silicone antifoaming agents have had storage stability problems. The silicone antifoaming agent separates from the concentrate and agglomerates on the storage container. This problem is exacerbated when the lubricants have lower levels (e.g., less than 2% by weight) of dispersants, such as reaction products of polyisobutenyl succinic anhydride and polyamines. This problem is especially exacerbated when the dispersant level is 0.5% or less in the lubricant or functional fluid.

To avoid these problems, lubricant additive concentrates have been blended without silicone antifoaming agents to avoid separation of the antifoaming agent from the concentrate and to avoid agglomeration in the storage container since silicone antifoaming agents are poorly soluble in mineral oil systems. When a lubricant additive concentrate has these undesirable characteristics, further blending with a majority of an oil of lubricating viscosity to produce lubricants or functional fluids results in lubricants

and functional fluids having unacceptable antifoaming properties.

In the past, because of storage stability problems, the antifoaming agent and the lubricant additive concentrate had to be each separately added to the oil of lubricating viscosity to form the lubricant or functional fluid. This method of blending therefore required the formulator to have a separate storage tank for the lubricant additive concentrate and for the antifoaming agent. Also, it required the formulator to perform two different mixing steps to blend the lubricant additive concentrate and antifoaming agent with the oil of lubricating viscosity. Furthermore, the separation and agglomeration problems of antifoaming agents would remain using this known blending method in making the lubricants and functional fluids due to incompatibility and solubility problems of silicone antifoaming agents with the oil of lubricating viscosity.

We have now found it possible to produce storage stable lubricant additive concentrates containing a silicone antifoaming agent using the method according to the present invention.

The storage stable lubricant additive concentrate made according to the present invention can be shipped, and then added to an oil of lubricating viscosity and, optionally, to viscosity modifiers, to produce lubricants or functional fluids having improved antifoaming properties.

The lubricants or functional fluids made from the lubricant additive concentrates made according to the present invention show improved antifoaming performance. Also, the lubricant additive concentrates according to the present invention do not exhibit storage problems, even after several months of storage.

Summary of the Invention

The present invention relates to a method for making a storage stable lubricant additive concentrate containing a silicone antifoaming agent comprising blending together components of the lubricant additive concentrate using a high-speed in-line mixer having a high-shear rotor/stator workhead and emulsor screen such that the antifoaming agent forms discrete micelles. The antifoaming agent is added to the mixer at a location before the workhead. The method according to the present invention provides for emulsification of the silicone antifoaming agent, enabling the antifoaming agent in the mixture to form micelles having a particle size of about 30 μ

or less.

The lubricants or functional fluids made from the storage stable lubricant additive concentrate made according to the method of the present invention have improved antifoaming performance, and the lubricant additive concentrates of the present invention exhibit storage stability, even after several months of storage.

Detailed Description of the Invention

Various preferred features and embodiments of the invention are hereinafter described by way of non-limiting illustration.

The method according to the present invention preferably utilizes a Silverson in-line mixer having a high-shear rotor-stator processing workhead fitted with an emulsor screen, with round orifices, having a diameter from about 0.015 to about 0.065 inches, preferably from about .025 to about 0.05 inches, most preferably a diameter of about 0.03 inches. Such a mixer enables the concentrate in the mixer, including the antifoaming agent, to form small, discrete micelles having a particle size of about 30 μ or less, preferably from about 10 μ to about 25 μ, most preferably about 20 μ. Here, and elsewhere in the specification and claims, the range and ratio limits may be combined. A micelle is a molecular aggregate of the concentrate that constitutes a colloidal particle. The antifoaming agent, due to the mixing according to the present invention, forms these discrete micelles.

The mixer utilized according to the present invention conveniently provides for hydraulic and mechanical shear to a material passing through it, wherein such shear results in smaller particle size of the material passing through it, and thus better dispersion, emulsification, and homogenization of the resultant composition.

According to the method of the present invention, several components used in making the lubricant additive concentrate may be first blended together. Then, the silicone antifoaming agent is added to the mixture at a location before the workhead, followed by further blending, using the mixer at high speed, generally under blending conditions at a given temperature, for a given time, to enable the silicone antifoaming agent to form micelles, to produce a storage stable lubricant additive concentrate.

The weight percentage or amount of each component set forth throughout this specification is on a diluent-free basis, unless otherwise indicated.

More specifically, the mixing apparatus used in making the lubricant additive

concentrate is preferably a high-speed in-line mixer manufactured and sold by Silverson Machines Ltd. of Waterside, England. It is a Silverson model 600LS, and mixes at a full mixer speed from about 1000 to about 6000 rpm. The phrase "full mixer speed" or "full mixing speed" as used throughout this specification means from about 1000 to about 6000 rpm. The emulsor screen provides for homogenization of the mixer. Such a mixer enables the silicone antifoaming agents to form small discrete micelles having a particle size of about 30 μ or less, preferably from about 15 μ to about 25 μ, most preferably of about 20 μ.

In the method according to the present invention, the silicone antifoaming agent is usually added at a rate not to exceed one batch volume through the mixer. The phrase "one batch volume" is a volume that passes through the mixer from a batch of mix. Therefore, the amount of silicone antifoaming agent added cannot exceed the amount of silicone antifoaming agent desired in one batch of mix that passes through the mixer.

The silicone antifoaming agents that can be used in the present invention can be silicone antifoaming agents that form micelles having the size as described above under the conditions of the method according to the present invention. Such silicone antifoaming agents can be polysiloxanes, also known as polydialkyl siloxanes. The polydialkyl siloxanes can be polydialkyl siloxane wherein each alkyl of the polydialkyl can independently have from 1 up to about 8 carbon atoms or from 1 up to about 12 carbon atoms, and can be independently a methyl, ethyl, propyl, butyl, or hexyl group. The polysiloxane alone, or polysiloxanes in combination, can have a viscosity of from about 20,000 to about 100,000 centistokes at 25°C, preferably from about 30,000 to about 80,000 centistokes at 25°C, most preferably from about 40,000 to about 60,000 centistokes at 25°C. The kinematic viscosity is based on a diluent-free basis.

In a first embodiment, the silicone antifoaming agent used is selected from

(a) a polydialkyl siloxane having a kinematic viscosity preferably from about 15,000 to about 45,000, more preferably from about 20,000 to about 35,000 centistokes at 25°C, most preferably from about 25,000 to about 30,000 centistokes at 25°C,

(b) a polydialkyl siloxane having a kinematic viscosity preferably from about 50,000 to about 150,000, more preferably from about 70,000 to about

115,000 centistokes at 25°C, most preferably from about 90,000 to about 110,000 centistokes at 25°C,

(c) a polydialkyl siloxane having a kinematic viscosity preferably from about 300 to about 2,000, more preferably from about 500 to about 1200 centistokes at 25°C, most preferably from about 900 to about 1100 centistokes at 25°C, and

(d) mixtures of two or more of (a), (b), and (c) thereof.

Component (a) is conveniently a 10 weight percent of the polydialkyl siloxane and 90 weight percent of an aliphatic hydrocarbon solvent, such as kerosene. Component (b) is conveniently a 12.5 weight percent of the polydialkyl siloxane and 87.5 weight percent of an aliphatic hydrocarbon solvent, such as kerosene. Component (c) is conveniently a 10 weight percent of the polydialkyl siloxane and 90 weight percent of an aliphatic hydrocarbon solvent, such as kerosene.

When the silicone antifoaming agent comprises components (a) and (b) only, (a) may be present in the silicone antifoaming agent in an amount from about 55 to about 85 weight percent, preferably from about 65 to about 75 weight percent on a diluent-free basis, and (b) may be present in the silicone antifoaming agent in an amount from about 15 to about 45 weight percent, preferably about 25 to about 35 weight percent on a diluent-free basis. If the weight percentage includes the diluent, i.e., if the weight percentage includes the aliphatic hydrocarbon solvent, such as kerosene, component (a) may be present in an amount from about 5.5 to about 8.5 weight percent, preferably from about 6.5 to about 7.5 weight percent, and component (b) may be present in an amount from about 13 weight percent to about 39 weight percent, preferably from about 22 weight percent to about 30 weight percent. The remainder of the weight percentage is the diluent.

In a second embodiment, the antifoaming agent can be a mixture of (a) a polydialkyl siloxane having a kinematic viscosity of about 20,000 to about 40,000, preferably about 25,000 to about 35,000 centistokes at 25°C, and (b) a polydialkyl siloxane having a kinematic viscosity of about 85,000 to about 115,000, preferably from about 90,000 to about 110,000 centistokes at 25°C. In this second embodiment, the silicone antifoaming agent is a mixture of (a) and (b), wherein the silicone antifoaming agent may be a combination of (a) and (b) in a weight ratio of about 0.82

to about 0.18, preferably from about 0.71 to about 0.29, respectively.

The silicone antifoaming agents are available from Dow Corning.

In another method according to the present invention, the lubricant additive concentrate is made by first providing a diluent oil, a friction modifier, and optionally a carboxylic solubilizer, followed by blending the diluent oil, the friction modifier, and the optional carboxylic solubilizer, using a high-speed in-line mixer having a workhead, and fitted with an emulsor screen; and then adding the silicone antifoaming agent at a location before the workhead, followed by blending for a period of time and at a temperature sufficient to emulsify the silicone antifoaming agent, to form an antifoaming agent-containing mixture.

The friction modifiers and the optional carboxylic solubilizer that can be utilized in the present invention are illustrated below.

Friction Modifiers

Friction modifiers include fatty oils and esters and sulfurized derivatives thereof, borated epoxides, borated esters, fatty amines and amides, and mixtures of two or more thereof.

The amount of friction modifier or combination of friction modifiers as used in the present invention may be from about 4 to about 12 weight percent, preferably from about 6 to about 10 weight percent, most preferably about 8.0 weight percent, based upon the total weight of the lubricant additive concentrate.

The fatty oils and esters generally contain carboxylic acids or derivatives thereof which have from about 8 to about 30, or from about 12 to about 24 carbon atoms. Examples of unsaturated fatty acids include palmitoleic acid, oleic acid, linoleic acid, linolenic acid, erucic acid, lard oil acid, soybean oil acid, tall oil acid and rosin acid. The unsaturated fatty esters include fatty oils, that is, naturally occurring or synthetic esters of glycerol and one or more of the above unsaturated fatty acids. Examples of fatty esters include animal fats, such as Neat's-foot oil, lard oil, depot fat, beef tallow, vegetable oils such as cottonseed oil, corn oil, safflower oil, sesame oil, soybean oil, and sunflower seed oil. The unsaturated fatty esters also may be prepared by esterifying a fatty acid with alcohols and polyols. The alcohols include mono- and polyhydric alcohols, such as methanol, ethanol, propanol, butanol, ethylene glycol, neopentyl glycol, glycerol and the like.

The above fatty oils and esters may be sulfurized by any means known to those in the art. U. S. Patents 3,926,822 and 3,955,347, both issued to Habiby, teach oils and sulfurized products made therefrom. These patents are incorporated by reference in their entirety.

In another embodiment, the friction modifier is a borated fatty amine. The borated amines are prepared by reacting one or more boron compounds, such as boric acid or ester thereof with one or more fatty amine, e.g., amines having from about four up to about thirty,, or from about eight to about eighteen carbon atoms. Fatty amines include n-octylamine, n-decylamine, n-dodecylamine, n-tetradecylamine, n-hexadecyl-amine, n-octadecylamine, oleyamine, cocoaamine, oleylamine, tallowamine, and stearylamine. For example, the borated fatty amines are prepared by reacting the amine with the boron compound at a temperature from about 50°C to about 300°C, preferably from about 100°C to about 250°C, and at a ratio from about 3:1 to about 1:3 equivalents of amine to equivalents of boron compound.

In another embodiment, the friction modifier is a borated epoxide. The borated fatty epoxides are generally the reaction product of one or more boron compounds with an epoxide or mixtures of epoxides, such epoxides having from about 8 up to about 30, preferably from about 12 up to about 20 carbon atoms. Examples of useful aliphatic epoxides include heptyl epoxide, octyl epoxide, oleyl epoxide, C_{14-16} epoxide, C_{14-18} epoxide and the like. The borated fatty epoxides are generally known and are disclosed in U.S. Patent 4,584,115. This patent is incorporated by reference for its disclosure of borated fatty epoxides and methods for preparing the same.

In one embodiment, the friction modifier is a borate ester. The borate esters may be prepared by reacting one or more boron compound with one or more alcohols, such as those containing from about 6 up to about 30, or from about 8 to about 24 carbon atoms. The methods of making such borate esters are known to those skilled in the art.

In another embodiment, the friction modifier is a fattyamide such as those having from about 8 to about 30, or from about 12 to about 20 carbon atoms. Fatty amides include dodecylamide, tetradecylamide, oleylamide, stearylamide, tallowamide, etc. Fatty amides and their preparation are known in the art.

<u>Carboxylic Solubilizers</u>

The amount of a carboxylic solubilizer or combination of carboxylic solubilizers may be from about 2 to about 10 weight percent, preferably from about 6 to about 8 weight percent, most preferably about 4.0 weight percent, based upon the total weight of the lubricant additive concentrate.

The carboxylic solubilizers that are useful in accordance with the present invention include the nitrogen-containing, phosphorus-free carboxylic solubilizers disclosed in U.S. Patents 4,329,249; 4,368,133; 4,435,297; 4,447,348; and 4,448,703. These patents are incorporated herein by reference in their entirety. Briefly, these carboxylic solubilizers are made by reacting (I) at least one carboxylic acid acylating agent having at least one hydrocarbyl-based substituent of at least about 12 to about 500 carbon atoms with (II) at least one (a) N-(hydroxyl- substituted hydrocarbyl) amine, (b) hydroxyl- substituted poly(hydrocarbyloxy) analog of said amine (a), or (c) mixtures of (a) and (b). Preferred acylating agents include the substituted succinic acids or anhydrides. Preferred amines include the primary, secondary and tertiary alkanol amines or mixtures thereof. In a particularly preferred embodiment of the present invention, the carboxylic solubilizer is the reaction product of a polyisobutenyl-substituted succinic anhydride with diethylenethanolamine or a mixture of diethylenethanolamine and ethanolamine.

After the antifoaming agent-containing mixture is formed as described above, the method according to the present invention further comprises optionally adding other lubricant additives such as antiwear agents, dispersants, detergents, and a polyalkenyl carboxylic acylating agent, in a third blending step, to form the lubricant additive concentrate. Examples of these functional additives are described below.

<u>Antiwear Agents</u>

The antiwear agents include metal salts and ashless derivatives of phosphorus compounds and dithiocarbamate compounds. The amount of antiwear agent or combination of antiwear agents may be from about 10 to about 40 weight percent, preferably from about 15 to about 35 weight percent, most preferably about 30 weight percent based upon the total weight of the lubricant additive concentrate.

In one embodiment, the phosphorus compound is a metal thiophosphate, preferably a metal dithiophosphate. The metal thiophosphates are prepared by reacting a metal base with one or more thiophosphorus acids. The thiophosphorus acid may be mono- or dithiophosphorus acids. The thiophosphorus acid may be prepared by

reacting one or more phosphorus sulfides, such as phosphorus pentasulfide, with one or more alcohol. Each alcohol generally contains from about 3 to about 30, or from about 3 to about 18, or from about 4 to about 12 carbon atoms. The metals are typically alkaline earth and transition metal salts of phosphoric acids, preferably dithiophosphoric acids. Examples of metal dithiophosphates include zinc isopropyl, methylamyl dithiophosphate, zinc isopropyl isooctyl dithiophosphate, barium di(nonyl) dithiophosphate, zinc di(cyclohexyl) dithiophosphate, copper di(isobutyl) - dithiophosphate, calcium di(hexyl) dithiophosphate, zinc isobutyl isoamyl dithiophosphate, and zinc isopropyl secondary-butyl dithiophosphate.

In another embodiment, the metal dithiophosphates are further reacted with one or more epoxides having from about 3 to about 18, or from about 3 to about 8 carbon atoms, preferably propylene oxide or butylene oxide. These reaction products are described in U.S. Patent 3,213,020; 3,213,021; and 3,213,022, issued to Hopkins et al. These patents are incorporated by reference for such description of the reaction products.

In another embodiment, the phosphorus compound is a metal salt of (a) at least one dithiophosphoric acid and (b) at least one aliphatic or alicyclic carboxylic acid. The dithiophosphoric acids are described above. The carboxylic acid may be a monocarboxylic or polycarboxylic acid, usually containing from 1 to about 3, or just one carboxylic acid group. The preferred carboxylic acids are those having the formula RCOOH, wherein R is a hydrocarbyl group, preferably free from acetylenic unsaturation. Generally, R contains from about 2 to about 40, or from about 3 to about 24, or from about 4 to about 12 carbon atoms. In one embodiment, R contains from about 4 to about 12, or from about 8 to about 12, or to about 8 carbon atoms. In one embodiment, R is an alkyl group. Suitable acids include the butanoic, pentanoic, hexanoic, octanoic, nonanoic, decanoic, dodecanoic, octodecanoic and eicosanoic acids, as well as olefinic acids such as oleic, linoleic, and linolenic acids, and linoleic dimer acid. A preferred carboxylic acid is 2-ethylhexanoic acid. U.S. Patents 4,308,154 and 4,417,990 describe procedures for preparing these metal salts and disclose a number of examples of such metal salts. These patents are hereby incorporated by reference for their disclosures.

In one embodiment, the phosphorus compound may be a reaction product of a phosphorus acid and an unsaturated compound. The unsaturated compounds include

unsaturated amides, esters, acids, anhydrides, and ethers. The phosphorus acids preferably are dithiophosphoric acids. In one embodiment, the phosphorus compound is a reaction product of a phosphorus reagent, such as a dithiophosphric acid, and an unsaturated compound. The thiophosphorus acid esters may be mono- or dithiophosphorus acid esters. Thiophosphorus acid esters are also referred to generally as dithiophosphates.

The reaction products of phosphoric acids and an unsaturated amide are referred to as phosphorus containing amides. An example of such reaction product is the reaction of methylamyl dithiophosphoric acid or isooctyl, isopropyl dithiophosphoric acid and acrylamide. The phosphorus containing amides are known in the art and are disclosed in U.S. Patents 4,670,169, 4,770,807, and 4,876,374 which are incorporated by reference for their disclosures of phosphorus amides and their preparation. Examples of reaction products of a phosphoric acid and an unsaturated ester are the reaction product of isobutyl, amyl dithiophosphoric acid and methyl acrylate and di(amyl)dithiophosphoric acid and butyl methacrylate.

In another embodiment, the antiwear agent is a metal containing or ashless dithiocarbamate. The metal-containing dithiocarbamates are prepared reacting a dithiocarbamic acid with a metal base. The metal base may be any metal compound capable of forming a metal salt. Examples of metal bases include metal oxides, hydroxides, carbonates, borates, or the like. These metals include the alkali metals, alkaline earth metals, and transition metals. In one embodiment, the metal is a Group IIA metal, such as calcium or magnesium, a Group IB metal, such as copper, a Group IIB metal, such as zinc, or a Group VIIB metal, such as manganese. Examples of metal containing dithiocarbamates zinc diamyldithiocarbamate, zinc di(2-ethylhexyl) dithiocarbamate, magnesium dibutyldithiocarbamate, magnesium dioctyldithiocarbamate, sodium diamyldithiocarbamate, and sodium diisopropyl dithiocarbamates. The metal dithiocarbamates and their preparation are described in U.S. Patent 4,612,129, which is incorporated by reference.

In another embodiment, the sulfur compound is an ashless dithiocarbamate. The ashless dithiocarbamate may be an amine salt of a dithiocarbamic acid and one or more amine. The dithiocarbamate compositions include reaction products of a dithiocarbamic acids or salts and an unsaturated amide, carboxylic acid, anhydride, ester, or ether and mixtures of two or more thereof. The dithiocarbamate

compositions may also be prepared by simultaneously reacting an amine, carbon disulfide and an unsaturated compound. U.S. Patents 4,758,362 and 4,997,969 describe dithiocarbamate compositions and methods of making the same. These patents are hereby incorporated by reference for their disclosure of dithiocarbamate compositions and method of making the same.

In one embodiment, the dithiocarbamate compound is prepared by reacting one or more of dithiocarbamic acids or salts with unsaturated reagents, such as unsaturated amides, unsaturated anhydrides, acids, or esters, unsaturated ethers. The unsaturated ethers contain from about 3 to about 30, or from about 4 to about 24 carbon atoms. The unsaturated ethers include methyl vinyl ether, propyl vinyl ether, 2-ethyl hexyl vinyl ether, and the like.

Detergents

The amount of detergent or combination of detergents may be from about 25 to about 70 weight percent, preferably from about 35 to about 65 weight percent based upon the total weight of the lubricant additive concentrate.

The detergents are exemplified by oil-soluble neutral and basic salts (i.e. overbased salts) of alkali or alkaline earth metals with sulfonic acids, carboxylic acids, phenols or organic phosphorus acids. The overbased compounds include basic salts (i.e., overbased salts) of alkali or alkaline earth metals with sulfonic acids, carboxylic acids, phenols or organic phosphorus acids. The phosphorus acids include those prepared by the treatment of a polyalkene with a phosphorizing agent, such as phosphorus pentasulfide. The most commonly used metals are sodium, potassium, lithium, calcium, and magnesium. The term "basic salt" is used to designate metal salts wherein the metal is present in stoichiometrically larger amounts than the organic acid radical. The overbased salt typically has a metal ratio from about 3 to about 40, or from about 5 to about 25. Examples of overbased salts include calcium or magnesium alkylbenzene sulfonic acid, and sodium alkylbenzene sulfonate or polyisobutenylsuccinnate.

The overbased salts and borated overbased salts may be prepared by means known to those in the art. Patents describing overbased salts, methods of making the salts and components for making the same include U.S. Patents 2,501,731; 2,616,911; 2,777,874; 3,384,585; 3,320,162; 3,488,284 and 3,629,109. The disclosure of these patents are hereby incorporated by reference.

The detergents may also be borated overbased metal compositions. Borated overbased compositions, lubricating compositions containing the same, and methods of preparing borated overbased compositions are found in U.S. Patents 4,744,920, 4,792,410, and PCT publication WO 88/03144. The disclosure of these references are hereby incorporated by reference.

Dispersants

The dispersants can include acylated amines, carboxylic esters, Mannich reaction products, hydrocarbyl substituted amines, and mixtures thereof. The amount of dispersant or combination of dispersants may be from about 0.1 to about 16.0 weight percent, preferably less than about 8.0 weight percent, based upon the total weight of the lubricant additive concentrate.

The acylated amines include reaction products of one or more carboxylic acylating agent and one or more amine. The carboxylic acylating agents include C_{8-30} fatty acids, and hydrocarbyl substituted carboxylic acylating agents. The hydrocarbyl substituted carboxylic acylating agents are prepared by a reaction of one or more of the olefins having from about 8 to about 30 carbon atoms or polyalkenes having an $\overline{M}n$ from about 500 to about 5,000 or from about 800 to about 2500 or from about 900 to about 2000, with one or more of unsaturated carboxylic reagents, such as acrylic acids or esters, methacrylic acid or esters, and maleic, fumaric or itaconic acids, and maleic anhydride. The amines include polyamines, such as alkylenepolyamines or condensed polyamines. Acylated amines, their intermediates and methods for preparing the same are described in U.S. Patents 3,219,666; 4,234,435; 4,952,328; 4,938,881; 4,957,649; 4,904,401; and 5,053,152. Those patents are hereby incorporated by reference in their entirety for such disclosure.

In another embodiment, the dispersant may also be a carboxylic ester. The carboxylic ester is prepared by reacting at least one or more of carboxylic acylating agents, preferably a hydrocarbyl substituted carboxylic acylating agent, with at least one organic hydroxy compound and optionally an amine. The hydroxy compound may be an alcohol or a hydroxy containing amine, such as alkanolamines. Preferred alcohols are polyhydric alcohols, such as glycerol, pentaerythritol, and derivatives of pentaerythritol. The preparation of useful carboxylic ester dispersant is described in U.S. Patents 3,522,179 and 4,234,435, and their disclosures are incorporated by

reference.

The carboxylic ester dispersant may be further reacted with at least one amine and preferably at least one polyamine, such as a polyethylenepolyamine, condensed polyamine, or a heterocyclic amine, such as aminopropylmopholine. These carboxylic ester dispersant compositions are known in the art, and the preparation of a number of these derivatives is described in, for example, U.S. Patents 3,957,854 and 4,234,435 which have been incorporated by reference previously.

In another embodiment, the dispersant may also be a hydrocarbyl-substituted amine. These hydrocarbyl-substituted amines are well known to those skilled in the art. These amines are disclosed in U.S. Patents 3,275,554; 3,438,757; 3,454,555; 3,565,804; 3,755,433 and 3,822,289. These patents are hereby incorporated by reference for their disclosure of hydrocarbyl amines and methods of making the same.

In another embodiment, the dispersant may also be a Mannich dispersant. Mannich dispersants are generally formed by the reaction of at least one aldehyde, such as formaldehyde and paraformaldehyde, at least one amine, preferably a polyamine, such as a polyalkylenepolyamine, and at least one alkyl substituted hydroxyaromatic compound. Mannich dispersants are described in the following patents: U.S. Patent 3,980,569; U.S. Patent 3,877,899; and U.S. Patent 4,454,059 (herein incorporated by reference for their disclosure to Mannich dispersant).

Products obtained by post-treating the carboxylic, amine or Mannich dispersant with such reagents are urea, thiourea, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds, phosphorus compounds or the like, may also be used.

In addition to the above-mentioned additives, a carboxylic acylating agent can also be added to the silicone antifoaming agent-containing mixture. The carboxylic acylating agents are as described above, and can be polyalkenyl carboxylic acylating agents. The amount of a polyalkenyl carboxylic acylating agent added according to the present invention is from about 0.1 to about 1.0 weight percent, preferably about 0.4 weight percent, based upon the total weight of the lubricant additive concentrate. An example of a carboxylic acylating agent is polyisobutenyl ($\overline{M}n$ about 1000) succinic anhydride.

Other Additives

The invention also contemplates the use of other additives. Such additives include, for example, corrosion- and oxidation-inhibiting agents, pour point depressing agents, extreme pressure agents, and color stabilizers. The amounts utilized are at typical use level.

Auxiliary extreme pressure agents and corrosion- and oxidation-inhibiting agents which may be included in the lubricants of the invention are exemplified by chlorinated aliphatic hydrocarbons such as chlorinated wax; sulfurized alkylphenol; phosphosulfurized hydrocarbons, such as the reaction product of a phosphorus sulfide with turpentine or methyl oleate; metal thiocarbamates, such as zinc dioctyldithiocarbamate, and barium diheptylphenyl dithiocarbamate. Many of the above-mentioned extreme pressure agents and corrosion- and oxidation-inhibitors also serve as antiwear agents.

Pour point depressants are an additive often included in the lubricating oils described herein. Examples of useful pour point depressants are polymethacrylates; polyacrylates; polyacrylamides; condensation products of haloparaffin waxes and aromatic compounds; vinyl carboxylate polymers; and polymers of dialkylfumarates, vinyl esters of fatty acids and alkyl vinyl ethers. Pour point depressants useful for the purposes of this invention, techniques for their preparation and their uses are described in U.S. Patents 2,387,501; 2,015,748; 2,655,479; 1,815,022; 2,191,498; 2,666,746; 2,721,877; 2,721,878; and 3,250,715 which are hereby incorporated by reference for their relevant disclosures.

The above-mentioned functional additives may be blended with the antifoaming agent-containing mixture to form the storage stable lubricant additive concentrate.

The first blending step is conveniently conducted at a temperature from about 65 to about 95°C for a period of time from about 20 to about 40 minutes. The second blending step may be conducted at a temperature from about 65 to about 95°C for a period of time from about 15 to about 60 minutes. The third blending step may be conducted from about 40 minutes to about 75 minutes. The mixer is operated at full speed, that is, at an rpm from about 1000 to about 6000, throughout the entire process. That is, every blending step is conducted at from about 1000 to about 6000 rpm.

In an embodiment of the present invention, the resultant storage stable lubricant additive concentrate made according to the method of the present invention contains

from about 0.1 to about 16 weight percent, preferably from about 8.0 weight percent, of reaction products of polyisobutenyl succinic and polyamine.

After the storage stable lubricant additive concentrate is made, it may be shipped in this form, and then blended in major amount of oil of lubricating viscosity to form a lubricant or functional fluid.

More specifically, the storage stable lubricant additive concentrate can later be blended into a majority of oil of lubricating viscosity, and, optionally viscosity modifiers, to form fully formulated functional fluids or lubricants. Typically, a fully formulated functional fluid will combine about 3 to about 10 percent by weight of storage stable concentrate in about 90 to about 97 weight percent oil of lubricating viscosity. Where viscosity modifiers are also included in the functional fluid, they comprise about 1 to about 10 weight percent of the functional fluid with the weight percent of oil of lubricating viscosity and concentrate adjusted accordingly.

The oil of lubricating viscosity includes natural or synthetic lubricating oils and mixtures thereof. Natural oils include animal oils, vegetable oils, mineral lubricating oils, and solvent or acid treated mineral oils. Synthetic lubricating oils include hydrocarbon oils (polyalpha-olefins), halo-substituted hydrocarbon oils, alkylene oxide polymers, esters of dicarboxylic acids and polyols, esters of phosphorus-containing acids, polymeric tetrahydrofurans and silicon-based oils. Unrefined, refined, and rerefined oils, either natural or synthetic, may be used in the compositions of the present invention. A description of oils of lubricating viscosity occurs in U.S. Patent 4,582,618 (column 2, line 37 through column 3, line 63, inclusive), herein incorporated by reference for its disclosure to oils of lubricating viscosity.

Multigrade lubricants may include a viscosity improver which is formulated with the oil of lubricating viscosity to provide the above lubricant grades. Useful viscosity improvers include polyolefins, such as ethylene-propylene copolymers, or polybutylene rubbers, including hydrogenated rubbers, such as styrene-butadiene or styrene-isoprene rubbers; or polyacrylates, including polymethacrylates. Preferably the viscosity improver is a polyolefin or polymethacrylate, more preferably polymethacrylate. Viscosity improvers available commercially include Acryloid™ viscosity improvers available from Rohm & Haas; Shellvis™ rubbers available from Shell Chemical; and Lubrizol 3174 available from The Lubrizol Corporation.

The following non-limiting Examples serve to illustrate the invention.

Example 1

Components used to prepare the lubricant additive concentrate comprising (1) diluent oil, and (2) a friction modifier are first mixed by circulating them through a Silverson in-line mixer to form a first mixture at a temperature from about 65 to about 95°C for a period of time from about 20 to about 40 minutes, at full mixing speed (from about 1000 to about 6000 rpm). To this first mixture, at a location before the workhead of the mixer, is added (4) a silicone antifoaming agent, in a second blending step, to form an antifoaming agent-containing mixture. The antifoaming agent is added over a period of time not faster than that required for a batch volume of said mixture to pass through the mixer. Blending continues at a temperature from about 65 to about 95°C, at full mixing speed, for a period of time from about 15 to about 60 minutes.

To the antifoaming-containing mixture is then added, in a third blending step, other components required to make the lubricant additive concentrate, while the same mixing speed and temperature are maintained. Blending is continued for about 30 minutes to about 2 hours. The added other components comprise antiwear agents, detergents and, optionally, dispersants.

The resultant storage stable lubricant additive exhibited little separation and/or agglomeration, even after up to about nine months or longer of storage.

Example 2

A 1000 kg batch of lubricant additive package concentrate was prepared using a Silverson Model 600LS in-line mixer with a power specification of 15KW. The mixer provides for both mechanical and hydraulic shear of the material passed through its workhead and employs a rotor/stator processing workhead identified as a standard emulsor screen with about 0.030 diameter round orifices. The mixer with the stated workhead produces micelles having a particle size of about 20μ.

The concentrate of this example of the present invention has a formula comprising:

(1) 5.43 weight percent 100 neutral diluent oil;

(2) 8.33 weight percent borated α-olefin epoxide friction modifier;

(3) 4.17 weight percent of a carboxylic solubilizer;

(4) 1.33 weight percent silicone antifoaming agents;

(5) 50 weight percent of an overbased calcium sulfonate detergent having 300 TBN and 53 weight percent diluent oil;

(6) 31.67 weight percent zinc dithiophosphate antiwear agent having 11 weight percent diluent oil content;

(7) 0.4 weight percent polyisobutenyl ($\bar{M}n$ about 1000) succinic anhydride.

Components (1) - (3) were blended in a first blending step at full speed (1000 to 6000 rpm) using a Model 600LS in-line mixer at about 80°C.

While temperature and mixing speed were maintained, the silicone antifoaming agents (4) were added to the mixture at a location before the workhead of said mixer at a rate not to exceed the passing of one batch of the mixture through the mixer workhead (about ten minutes). Silicone antifoaming agents (4) are a combination of 0.094 weight percent polydimethyl siloxane at 30,000 centistokes at 25°C and 0.049 weight percent polydimethyl siloxane at 100,000 centistokes at 25°C. The mixture containing components (1) - (4) was then further mixed in a second blending step for about thirty minutes at full speed of the mixer at about 80°C.

Following addition of the antifoaming agent, while mixing speed and temperature (about 80°C) were maintained, the other components comprising (5) an antiwear agent, (6) a detergent and, optionally, (7) a carboxylic acylating agent were added, in a third blending step, to the antifoaming agent-containing mixture. Following the addition of (5), (6) and (7), the mixture was further mixed at the same temperature, for about 0.5 to about 2 hours, at the same speed of the in-line mixer, to produce a storage stable lubricant additive concentrate.

For illustrative purposes, the following Tables 1 and 2 show the various combinations of components that may be utilized according to the method of the present invention. Table 1 sets forth the diluent oil component, the friction modifier component, the silicone antifoaming agent component, and the solubilizer that can be used to form the silicone antifoaming agent-containing mixture. Table 2 sets forth the antiwear agents, detergents, and polyisobutenyl succinic anhydride which are added after formation of the silicone antifoaming agent-containing mixture made from the

components from any one of the columns from Table 1. The numbers in Tables 1 and 2 represent weight percentages on an oil-free basis (no diluent), unless otherwise indicated, based upon the total weight of the lubricant additive concentrate.

For illustrative purposes, Table 1, column A, sets forth that the 0.6 weight percent of polydimethylsilixane, 6.2 weight percent of glycerol monooleate, 2.0 weight percent of diluent oil, and 10 weight percent carboxylic solubilizer are mixed to form the silicone antifoaming agent-containing mixture. This column of components can then be mixed with a column of components in Table 2 to form the lubricant additive concentrate.

Table 1

	A	B	C	D	E	F	G	H
Polydimethylsiloxane A (1)	-	0.9	1	0.4	-	0.3	-	0.9
B (2)	0.6	0.4	-	-	-	-	0.8	0.4
C (3)	0.8	-	-	0.4	-	-	0.9	-
D(4)	-	-	-	-	1.8	0.4	-	-
Glycerol monooleate	6.2	-	-	-	-	7.0	-	-
Borated C_{16} epoxide	-	8.3	4.1	-	-	-	-	8.3
Oleylamide	-	-	-	3	8.3	-	-	-
Sulfurized lard oil	-	-	8.3	-	-	2	-	-
Diluent oil (1000 N Mineral Oil)	2	6	15	8	7	3.2	9	5.4
Carboxylic Solubilizer (5)	10	4.2	7.5	6	4.2	8	3.5	4.2

(1) 10% of a polydimethyl siloxane (Kinematic Viscosity of 30,000 cSt at 25°C in kerosene)
(2) 12.5% of a polydimethyl siloxane (Kinematic Viscosity of 100,000 cSt at 25°C in kerosene)
(3) 10% of a polydimethyl siloxane (Kinematic Viscosity of 1,000 cSt at 25°C in kerosene)
(4) 10% of a polydimethyl siloxane (Kinematic Viscosity of 50,000 cSt at 25°C in kerosene)
(5) Reaction product of polyisobutenyl ($\overline{M}$n about 1000) succinic anhydride and diethylethanolamine

Table 2

	I	J	K	L	M	N
Zinc dithiophosphate	28.2	-	-	-	-	-
Zinc dithiocarbanate	-	27.8	-	-	-	-
Mixed zinc carboxylate dithiophosphate	-	-	28.2	14	-	-
Sulfurized isobutylene	-	-	-	15	-	-
Overbased calcium sulfonate having 300 TBN and 53% weight diluent oil	-	-	50	-	69	-
Overbased magnesium sulfonate having 400 TBN and 42% weight diluent oil	25	-	-	45	-	-
Polyisobutenyl ($\overline{M}$n about 1000) succinic anhydride	-	-	0.4	0.2	-	-
Reaction product of polyisobutenyl succinic anhydride and polyethyl polyamine	-	16	-	6	-	-

The storage stable lubricant additive concentrate can then be shipped, and later added to a majority of oil of lubricating viscosity, and, optionally, viscosity modifiers, to obtain a lubricant or functional fluid. Fully formulated functional fluids may also typically contain anti-oxidants, corrosion inhibitors, rust inhibitors, pour-point depressants, rust inhibitors and seal swell agents.

The foaming characteristics of functional fluids and lubricants made from the storage stable lubricant additive concentrates according to the present invention were determined using ASTM D892, Sequence II.

The concentrates are blended as Esso J20C formulations. The Esso J20C formulations comprise 44.04 weight percent Esso 150N, 44.04 weight percent Esso 90N, 0.71 weight percent Lubrizol 7077 viscosity modifier available at the Lubrizol Corporation and 0.21 weight percent Lubrizol 7749B pour-point depressant, available at Lubrizol Corporation. To this mixture was added the lubricant additive concentrate according to the present invention at 6 weight percent. The added lubricant additive concentrate was the lubricant additive concentrate produced in Example 2, wherein the antifoaming agent was a combination of antifoaming agents (a) and (b) in a weight ratio of about 0.71 and about 0.29, respectively.

The functional fluids obtained after mixing the lubricant additive concentrate with an oil of lubricating viscosity passed the John Deere J20C/D foaming test of 50/0 (ml), even after nine months of storage of the concentrate prior to blending with the oil of lubricating viscosity.

Also, the J20C formulations passed the John Deere Sequence II test when blended with the lubricant additive concentrate that was stored for several months prior to testing, and still passed the John Deere J20C/D foaming test.

While the mixer discussed herein is a Silverson in-line mixer, any mixing system which provides sufficient shear enables the antifoaming agent to form micelles having a particle size of about 30 μ or less, preferably from about 10 μ to about 25 μ, most preferably about 20 μ, that results in a composition which homogenizes better, may be used.

While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those

skilled in the art upon reading the specification.

CLAIMS:

1. A method for making a storage stable lubricant additive concentrate containing a silicone antifoaming agent, comprising:

blending together components of said lubricant additive concentrate using a high-speed in-line mixer having a high-shear rotor-stator workhead and emulsor screen, such that said antifoaming agent forms discrete micelles,

wherein said blending is accomplished by adding said antifoaming agent at a location in front of said workhead.

2. The method according to claim 1, wherein said high-speed in-line mixer is a Silverson in-line mixer having a high-shear rotor-stator processing workhead fitted with an emulsor screen which has round orifices having a diameter from about 0.015 to about 0.065 inches.

3. The method according to claim 1 or claim 2, wherein said in-line mixer is a Silverson model 600LS and mixes at a mixer speed from about 1000 to about 6000 rpm.

4. The method according to any preceding claim, wherein said antifoaming agent is added at a rate not to exceed one batch volume through said mixer.

5. The method according to any preceding claim, wherein said antifoaming agent is selected from

(a) a polydialkyl siloxane having a kinematic viscosity from about 15,000 to about 45,000 centistokes at 25°C,

(b) a polydialkyl siloxane having a kinematic viscosity from about 50,000 to about 150,000 centistokes at 25°C,

(c) a polydialkyl siloxane having a kinematic viscosity from about 300 to about 2,000 centistokes at 25°C, and

(d) mixtures of two or more of (a), (b), and (c) thereof.

6. The method according to any preceding claim, wherein said antifoaming agent is a mixture of (a) a polydialkyl siloxane having a kinematic viscosity of about 20,000 to about 40,000 centistokes at 25°C and (b) a polydialkyl siloxane having a kinematic viscosity from about 85,000 to about 115,000 centistokes at 25°C.

7. The method according to claim 5 or claim 6, wherein said antifoaming agent comprises components (a) and (b), wherein (a) is present in an amount from about 55 to about 85 weight percent and (b) is present in an amount from about 15 to about 45 weight percent, on a diluent-free basis, based upon the total weight of said silicone antifoaming agent.

8. The method according to any preceding claim, wherein said lubricant additive concentrate contains from about 0.1 to about 16.0 weight % of reaction products of polyisobutenyl succinic anhydride reacted with polyamines.

9. The method according to any preceding claim, wherein said lubricant additive concentrate contains less than about 8.0 weight % of reaction products of polyisobutenyl succinic anhydride reacted with polyamines.

10. The method according to any preceding claim, wherein said lubricant additive concentrate is then blended in a majority of oil of lubricating viscosity to form a functional fluid or lubricant.

11. A method of making a lubricant additive concentrate, comprising:

(a) providing a diluent oil, a friction modifier, and a silicone antifoaming agent,

(b) blending said diluent oil and said friction modifier to form a first mixture, using a high-speed in-line mixer having a workhead; and

(c) adding said silicone antifoaming agent at a location before said workhead of said high-speed in-line mixer,

(d) blending for a period of time and at a temperature sufficient to emulsify said silicone antifoaming agent, to form an antifoaming agent-containing mixture.

12. The method according to claim 11, further comprising:

adding to said antifoaming agent-containing mixture, while blending continues, functional additives to form said lubricant additive concentrate.

13. The method according to claim 11 or claim 12, wherein step (b) is conducted at a temperature from about 65°C to about 95°C for a period of time from about 20 to about 40 minutes.

14. The method according to any one of claims 11 to 13, wherein step (d) is conducted at a temperature from about 65 to about 95°C for a period of time from about 15 to about 60 minutes.

15. The method according to any one of claims 11 to 14, wherein said high-speed in-line mixer operates at 1000 to 6000 rpm, using a high-shear rotor/stator processing workhead, and is fitted with a standard emulsor screen.

16. The method according to any one of claims 11 to 15, wherein said lubricant additive concentrate is then blended in a majority of oil of lubricating viscosity to form a functional fluid or lubricant.

17. A lubricant additive concentrate, comprising: (a) an additive for a lubricant additive concentrate, and (b) a silicone antifoaming agent present in said lubricant additive composition in micelles having a particle size of about 30 μ or less, preferably from about 15 μ to about 25 μ, and most preferably of about 20 μ.

18. A lubricant comprising a major amount of an oil of lubricating viscosity and a lubricant additive concentrate made by the method of any one of claims 1 to 16.

19. A lubricant comprising a major amount of an oil of lubricating viscosity and said lubricant additive concentrate of claim 17.

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Application No: GB 9904022.2
Claims searched: 1-19

Examiner: Dr William Thomson
Date of search: 18 May 1999

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.Q): C5F (FKG)

Int Cl (Ed.6): C10M 155/02

Other: ONLINE:CAS-ONLINE, EPODOC, JAPIO, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	GB 2072691A (EXXON) See whole document, in particular page 1, lines 46-56 and the claims.	
X	WPI Abstract Accession No 88-252628/25 & JP 630182008 (SHINETSU CHEM IND CO LTD) See abstract	1 at least
A	WPI Abstract Accession No 85-259382/42 & JP 600172315 (SHINETSU CHEM IND CO LTD) See abstract	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
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